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A ξ-Vector Formulation of Anisotropic Phase-Field Models: 3-D Asymptotics

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Abstract

In this paper we present a new formulation of a large class of phase-field models, which describe solidification of a pure material and allow for both surface energy and interface kinetic anisotropy, in terms of the Hoffman-Cahn ξ-vector. The ξ-vector has previously been used in the context of sharp interface models, where it provides an elegant tool for the representation and analysis of interfaces with anisotropic surface energy. We show that the usual gradient-energy formulations of anisotropic phase-field models are expressed in a natural way in terms of the ξ-vector when appropriately interpreted. We use this new formulation of the phase-field equations to provide a concise derivation of the Gibbs-Thomson-Herring equation in the sharp-interface limit in three dimensions.

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1. Introduction

The presence of surface energy anisotropy in the solidification of a pure material is a phenomenon of both practical and theoretical importance. In practice it leads to non-spherical equilibrium shapes, which, if the anisotropy is sufficiently pronounced, may exhibit missing orientations (e.g., edges or corners) or facets (flat surfaces). Its importance has been recently highlighted by the suggestion that it may be responsible for the selection of the dendrite tip operating state in the growth of a dendrite, see [1] for a review. Computations of dendritic growth using the phase-field method in two dimensions also suggest that surface energy anisotropy is an important effect in dendritic growth [2, 3, 4]. Various ad hoc modifications to phase-field models have been proposed to represent surface energy anisotropy. However, only for the model proposed by Kobayashi [3] is the corresponding boundary condition for the interfacial temperature in the sharp interface limit known and then only for an interface represented as a one-dimensional curve, see [5]. In reality, dendrites are three-dimensional and a sharp interface model requires the representation of their interfaces as two-dimensional surfaces. A phase-field model can also provide a setting for computation of three-dimensional dendrites, see [6]. In order to assess such computations it is important to know the free-boundary problem approached in the sharp interface limit. It is the aim of this paper to address this issue.

In this paper we provide a new formulation of a class of phase-field models that allow anisotropic surface energy and interface kinetics in terms of the Hoffman-Cahn ξ-vector [7, 8]. We exploit this representation to show that in the sharp-interface limit these phase-field models yield, at leading order, a free boundary problem in three dimensions which correctly accounts for the surface energy and kinetic anisotropy. In a previous paper [5] we derived the corresponding result in two dimensions for a specific phase-field model using a rather lengthy asymptotic analysis. In contrast, the ξ-vector formulation we develop here allows for a concise derivation in three dimensions of a whole class of anisotropic phase-field models.

Hoffman and Cahn [7] introduced the notion of a ξ-vector to represent the anisotropic surface energy of a sharp interface separating two phases. It provides a particularly elegant and useful device to describe an interface with an anisotropic surface energy, $\gamma(\vec{n})$, where $\vec{n}$ is the unit normal vector to the interface. It yields a succinct form of the equation for the interfacial temperature, T_I,

$$T_I = T_M - \frac{T_M}{L} \nabla_S \cdot \vec{\xi}, \qquad (1)$$

which can be shown to be equivalent to the classical Gibbs-Thomson-Herring equation; here we have neglected the effects of interface kinetics, which we consider in more detail below. T_M is the melting

temperature, L is the latent heat of fusion per unit volume and $\nabla_S \cdot \vec{\xi}$ is the surface divergence operator in the interfacial surface S applied to the ξ-vector. The surface divergence of the ξ-vector is equivalent to the notion of generalised mean curvature, as discussed by Taylor et al. [9, 10]. For the case of a two-dimensional geometry this reduces to the well-known form [11]

$$T_I = T_M - \frac{T_M}{L}(\gamma + \gamma_{\varphi\varphi})\mathcal{K},\qquad(2)$$

where φ is the angle of the normal $\vec{n}$ of the interface to a fixed direction, and $\mathcal{K}$ is the local curvature of the interface.

Various modifications to phase-field models to allow for surface tension anisotropy have been suggested. Langer [12] proposed including terms of squares of higher derivatives of the phase field and gave an example leading to cubic anisotropy. Caginalp and Fife ([13], see also [14]) suggested that the square gradient term that appears in the free-energy functional could be replaced by a more general quadratic form with different coefficients in each coordinate direction. A different approach is to include nearest neighbour interactions in a discrete formulation of a diffuse interface, see Cahn and Kikuchi [15]. More recently Kobayashi [3] and Wheeler et al. [2] have allowed the coefficient of the gradient energy to depend on the local orientation of the gradient of the phase field. An asymptotic analysis corresponding to the sharp interface limit in two dimensions was conducted by McFadden et al. [5] to show that the appropriate form of the boundary condition for the interfacial temperature was obtained.

In section 2 we briefly review the Cahn-Hoffman theory of the ξ-vector for a sharp interface. In section 3 we show how the ξ-vector arises in a natural way for a class of anisotropic phase-field models. In section 4 we examine a sharp interface limit of the anisotropic phase-field equations and recover the Gibbs-Thomson-Herring equation. Conclusions are given in section 5. Some technical points are relegated to appendices, which contain summaries of the relevant differential geometry and asymptotic expansions that are employed in the body of the paper.

2. The Hoffman-Cahn ξ-vector

Here we briefly review the elements of the theory of the ξ-vector given by Hoffman and Cahn [7].

For an isotropic surface energy γ, the equilibrium shape of a solid particle surrounded by its melt is described by a form of the Laplace-Young equation

$$\gamma\mathcal{K} = \Delta F,\qquad(3)$$

where $\mathcal{K}$ is the local mean curvature of the solid/liquid interface and the constant ΔF is the difference in the bulk free energies between the liquid and solid phases. The Laplace-Young equation can be derived by minimizing the surface energy subject to a volume constraint. The equation may also be written in terms of the surface divergence,

$$\nabla_S \cdot (\gamma \vec{n}) = \Delta F, \tag{4}$$

where $\vec{n}$ is the local normal to the interface. Properties of the surface differential operator ∇_S are reviewed in Appendix A; the property relevant here is that $\nabla_S \cdot \vec{n} = \mathcal{K}$.

In the anisotropic case, the surface tension of the solid/liquid interface depends on the local orientation of the interface, which can be expressed as a functional dependence of the the surface tension on the local unit normal to the interface, viz., $\gamma = \gamma(\vec{n})$. Cahn and Hoffman show that from the function $\gamma(\vec{n})$ a vector $\vec{\xi}$ can be defined such that the anisotropic version of Eq. (4) which governs equilibrium shapes has the form

$$\nabla_S \cdot \vec{\xi} = \Delta F; \tag{5}$$

the ξ-vector reduces to the vector $\gamma \vec{n}$ if γ is constant. Cahn and Hoffman give a formal definition of the ξ-vector in the form

$$\vec{\xi} = \nabla \left(r \hat{\gamma}(\theta, \varphi) \right); \tag{6}$$

here we have expressed the normal vector in terms of the spherical coordinates θ and φ, and have written $\hat{\gamma}(\theta, \varphi) = \gamma\left(\vec{n}(\theta, \varphi)\right)$. The gradient appearing in Eq. (6) is explicitly given by the expression

$$\vec{\xi} = \hat{\gamma}\vec{r} + \frac{\partial \hat{\gamma}}{\partial \theta}\vec{\theta} + \frac{1}{\sin\theta}\frac{\partial \hat{\gamma}}{\partial \varphi}\vec{\varphi}, \tag{7}$$

where $\vec{r}$, $\vec{\theta}$, and $\vec{\varphi}$ are unit vectors in the coordinate directions. It should be emphasised that the unit vectors $\vec{r}$, $\vec{\theta}$, and $\vec{\varphi}$ belong to a coordinate system associated with a specific point on the interface, and are used to describe vectors based at that point. In particular, in this coordinate system the normal to the interface is given by $\vec{n}(\theta, \varphi) = \vec{r}(\theta, \varphi)$, so that the normal component of the ξ-vector is given by γ, as in the isotropic case. In the anisotropic case, $\vec{\xi}$ also has components that lie in the plane tangent to the surface, which is spanned by the unit vectors $\vec{\theta}$ and $\vec{\varphi}$.

In the above definition the ξ-vector is parametrised by the spherical coordinates of the normal vector to the interface, with $\vec{\xi} = \vec{\xi}(\theta, \varphi)$. If the equilibrium shape is smooth and convex, then the angles θ and φ can themselves be used in a parametric description of the interface itself; that is, the interface can be expressed in the form $\vec{x} = \vec{x}(\theta, \varphi)$, where θ and φ range over the unit sphere. Although this appears to be a highly implicit description, since the interface shape is parametrised in

terms of its normal, it leads to an explicit expression for the interface shape. This follows from the identity (see Appendix A)

$$\nabla_S \cdot \vec{x} = 2, \tag{8}$$

stating that the surface divergence of the position vector of the interface is two. Comparing Eq. (5) and Eq. (8), we see that the interface shape can expressed in the form

$$\vec{x} = \frac{2}{\Delta F} \vec{\xi}. \tag{9}$$

Thus the ξ-vector actually provides an *explicit* parametric description of the equilibrium shape determined by $\gamma(\vec{n})$.

That the argument of $\gamma(\vec{n})$ is constrained to be a unit vector can be a complication when taking variations of the surface energy; this is one reason for introducing $\hat{\gamma}(\theta, \varphi)$. As pointed out by Taylor et al. [9, 10], a convenient alternative is to extend the domain of definition of the function $\gamma(\vec{n})$ from unit vectors to vectors $\vec{p}$ of arbitrary magnitude by setting

$$\gamma(\vec{p}) = |\vec{p}|\gamma(\vec{p}/|\vec{p}|), \tag{10}$$

which extends γ as a homogeneous function of first degree. With this extension, the function $r\hat{\gamma}(\theta, \varphi)$ used in the above definition (6) of the ξ-vector is given by

$$r\hat{\gamma}(\theta, \varphi) = r\gamma(\vec{n}) = \gamma(r\vec{n}), \tag{11}$$

which leads to the definition

$$\xi_j(\vec{p}) = \frac{\partial \gamma(\vec{p})}{\partial p_j}, \tag{12}$$

which is valid for vectors $\vec{p}$ of arbitrary length. For example, if the interface is expressed as a level set $\phi(\vec{x}) = $ constant, then the vector $\vec{p}$ with components

$$p_j = \frac{\partial \phi}{\partial x_j} \tag{13}$$

is proportional to the normal vector, and the surface tension is given by $\gamma = \gamma(\nabla \phi)$; Eq. (12) then defines $\vec{\xi} = \vec{\xi}(\nabla \phi)$.

Since $\gamma(\vec{p})$ is a homogeneous function of first degree, it satisfies the identity

$$\gamma(\vec{p}) = p_j \frac{\partial \gamma(\vec{p})}{\partial p_j} = \vec{p} \cdot \vec{\xi}(\vec{p}), \tag{14}$$

which results from differentiating the expression $\gamma(\lambda \vec{p}) = \lambda \gamma(\vec{p})$ with respect to λ and setting $\lambda = 1$. We note that here and throughout this paper we employ the Einstein summation convention with

the dummy indices ranging from one to three. Differentiating the expression $\gamma = \vec{p} \cdot \vec{\xi}$ and using the definition Eq. (12) to obtain

$$d\gamma = \vec{\xi} \cdot d\vec{p}, \tag{15}$$

results in the expression

$$\vec{p} \cdot d\vec{\xi} = 0, \tag{16}$$

Cahn and Hoffman use the fundamental relations (15) and (16) to provide a physical interpretation of the ξ-vector. They show that $-\vec{\xi}$ represents a force exerted by an elemental area of the interface which acts to rotate and contract the element in such a manner as to reduce its free-energy. In particular, the component of $\vec{\xi}$ in the direction $\vec{n}$ acts to reduce the area of the element without rotation and the component orthogonal to $\vec{n}$ acts to rotate the element without contraction of its area.

Just as the surface divergence of the ξ-vector replaces the term $\gamma \mathcal{K}$ in the Laplace-Young equation, the isotropic Gibbs-Thomson equation

$$T = T_M - \frac{T_M}{L} \gamma \mathcal{K} \tag{17}$$

assumes the form

$$T = T_M - \frac{T_M}{L} \nabla s \cdot \vec{\xi} \tag{18}$$

in the anisotropic case; the main goal of the present paper is to establish that this equation is recovered in an appropriate sharp-interface limit of a wide class of anisotropic phase-field models.

We note that Hoffman and Cahn were able to relate the equilibrium shape given by Eq. (9) to the Gibbs-Wulff construction that also gives the shape of equilibrium interface. In addition, Cahn and Hoffman extended this theory, in a very natural manner, to the situation where the anisotropy of the surface energy is so severe that the equilibrium interface suffers missing orientations or facets.

3. ξ-vector Formulation of Phase-Field Models

In this section we show how the ξ-vector arises in a natural way in a broad class of anisotropic phase-field models. Many phase-field models for the solidification of a pure material consist of a thermal diffusion equation coupled to a form of modified Cahn-Allen equation whose double well minima have depths that vary with temperature. Specific models differ in the form of bulk free energy density that is employed, and in the particular convention used to normalise the bulk values assumed by the phase-field function. In the sharp interface limit, the asymptotic analysis of the thermal diffusion equation produces the usual interfacial jump conditions for the temperature field, consisting of the

continuity of temperature and the balance of latent heat generation by the jump in heat flux across the interface. The modified Cahn-Allen equation produces the condition for thermal equilibrium, including the Gibbs-Thomson effect and the effect of interface kinetics. For our purposes it suffices to limit the discussion to the treatment of the modified Cahn-Allen equation only, and for simplicity we derive the equation from a relatively uncomplicated form of Helmholtz free energy functional. The specific form of free energy density that is employed is unimportant to the discussion, because in these models the surface tension anisotropy is produced through the choice of gradient energy expression in the free-energy functional.

We consider a Helmholtz free energy functional having the form

$$\mathcal{F} = \int_V \left\{ \frac{\eta^2}{2} |\nabla \phi|^2 + \frac{1}{4a} G(\phi) - \frac{L(T - T_M)}{T_M} P(\phi) \right\} dV, \tag{19}$$

where

$$G(\phi) = \phi^2 (1 - \phi)^2, \qquad P(\phi) = \phi^2 (3 - 2\phi), \tag{20}$$

η is the gradient energy coefficient and $1/a$ is proportional to the barrier height of the double-well potential. Here the phase field assumes the values $\phi = 0$ and $\phi = 1$ in the solid and liquid phases, respectively, and the function $P(\phi)$ varies monotonically from $P(0) = 0$ to $P(1) = 1$. The gradient energy coefficient η is constant in the isotropic case. The governing equation for ϕ is then assumed to have the form

$$\frac{1}{m} \frac{\partial \phi}{\partial t} = -\frac{\delta \mathcal{F}}{\delta \phi} = \eta^2 \nabla^2 \phi - \frac{1}{4a} G'(\phi) + \frac{L}{T_M} (T - T_M) P'(\phi), \tag{21}$$

where m is a mobility that is also constant in the isotropic case. For $T = T_M$ the equation admits a steady one-dimensional solution

$$\phi(x) = \frac{1}{2} \left\{ \tanh \left(\frac{x}{2\sqrt{2}[\eta\sqrt{a}]} \right) + 1 \right\}, \tag{22}$$

that represents a stationary planar solid/liquid interface with a thickness that can be characterised by the width

$$\delta = 2\sqrt{2}[\eta\sqrt{a}]. \tag{23}$$

The interface has a surface energy γ given by

$$\gamma = \int_{-\infty}^{\infty} \left\{ \frac{\eta^2}{2} \phi_x^2 + \frac{1}{4a} G(\phi) \right\} dx = \frac{(\eta\sqrt{a})}{6\sqrt{2}a}, \tag{24}$$

which is proportional to the product of the interface thickness and the energy per unit volume $1/a$ associated with the double-well barrier height.

For $T \neq T_M$ the equation admits a one-dimensional traveling-wave solution [16]

$$\phi(x,t) = \frac{1}{2}\left\{\tanh\left(\frac{x-Vt}{\delta}\right) + 1\right\}, \tag{25}$$

where the velocity is proportional to $(T_M - T)$,

$$V = \frac{6\sqrt{2}m[\eta\sqrt{a}]L(T_M - T)}{T_M}. \tag{26}$$

The form of this relation suggests that the mobility parameter m can be related to the interface kinetic coefficient μ by

$$\mu = \frac{6\sqrt{2}m[\eta\sqrt{a}]L}{T_M}, \tag{27}$$

a result which can also be established through a sharp-interface limit such as considered below.

The free energy functional can be rewritten in the form

$$\frac{\mathcal{F}}{L} = \int_V \left\{36[aL]\frac{\gamma^2}{L^2}|\nabla\phi|^2 + \frac{1}{4[aL]}G(\phi) - P(\phi)u\right\}dV, \tag{28}$$

where $u = (T-T_M)/T_M$ is the temperature relative to the melting point in units of T_M. The isotropic governing equation can then be written in the form

$$\frac{72[aL]}{T_M\mu}\left(\frac{\gamma}{L}\right)\frac{\partial\phi}{\partial t} = 72[aL]\frac{\gamma^2}{L^2}\nabla^2\phi - \frac{1}{4[aL]}G'(\phi) + P'(\phi)u. \tag{29}$$

The sharp-interface limit corresponds to the case that the diffuse interface width is small compared to a characteristic macroscopic length scale R, which can be taken to represent a typical radius of interfacial curvature in the nonplanar case. We consider the distinguished limit $\eta\sqrt{a}/R \to 0$ and $aL \to 0$, while maintaining a finite value for the ratio $\eta/\sqrt{a}$ in order that the surface energy remains finite in the limit.

It is convenient to measure length in units of R and energy density in units of L, in which case the free energy functional has the form

$$\mathcal{F} = \int_V \left\{36\epsilon\gamma^2|\nabla\phi|^2 + \frac{1}{4\epsilon}G(\phi) - P(\phi)u\right\}dV, \tag{30}$$

where $\epsilon = aL$ plays the role of a small parameter in the subsequent asymptotic treatment. We choose a diffusive time scale τ consistent with the accompanying thermal diffusion processes, and scale the dimensional kinetic coefficient in units of $R/(\tau T_M)$; the specific choice of time scale is unimportant to the discussion provided that the resulting dimensionless kinetic coefficient can be assumed to be of order unity. The dimensionless governing equation then has the form

$$\frac{72\epsilon\gamma}{\mu}\frac{\partial\phi}{\partial t} = 72\epsilon\gamma^2\nabla^2\phi - \frac{1}{4\epsilon}G'(\phi) + P'(\phi)u. \tag{31}$$

To formulate an anisotropic model in which the surface energy depends on orientation, Kobayashi [4] defines a normal vector ν to the level curves of the phase field at each point in space by setting

$$\vec{\nu} = \frac{\nabla \phi}{|\nabla \phi|} \tag{32}$$

and inserts the function $\gamma(\nabla \phi / |\nabla \phi|)$ in the relation (24) to obtain a gradient energy coefficient η that depends on the orientation of the level curves of ϕ. However, by expressing the free energy functional directly in terms of γ as in Eq. (30), and employing the homogeneous extension of γ, with

$$|\nabla \phi| \gamma \left(\frac{\nabla \phi}{|\nabla \phi|} \right) = \gamma(\nabla \phi), \tag{33}$$

the energy functional can be expressed in the form

$$\mathcal{F} = \int_V \left\{ 36\epsilon [\gamma(\nabla \phi)]^2 + \frac{1}{4\epsilon} G(\phi) - P(\phi)u \right\} dV. \tag{34}$$

In this form it is straightforward to take the variation of the functional to obtain

$$\frac{\delta \mathcal{F}}{\delta \phi} = -72\epsilon \frac{\partial}{\partial x_k} \left(\gamma \frac{\partial \gamma}{\partial \phi_{x_k}} \right) + \frac{1}{4\epsilon} G'(\phi) - P'(\phi)u. \tag{35}$$

We note the occurrence of the ξ-vector, with components $\xi^k = \partial \gamma / \partial \phi_{x_k}$, in the above expression. The anisotropic form of the dimensionless governing equation can therefore be written in the form

$$\frac{72\epsilon \gamma(\nabla \phi)}{\mu(\nabla \phi)} \frac{\partial \phi}{\partial t} = 72\epsilon \nabla \cdot (\gamma \vec{\xi}) - \frac{1}{4\epsilon} G'(\phi) + P'(\phi)u; \tag{36}$$

here we have assumed that $\gamma(\vec{p})$ and $\mu(\vec{p})$ are homogeneous functions of first degree in order to include the effects of both surface tension anisotropy and kinetic anisotropy.

We note that in this notation the anisotropy suggested by Caginalp and Fife [13] can be expressed in the simple form $\gamma(\nabla \phi) = \sqrt{(\eta_1 \phi_{x_1})^2 + (\eta_2 \phi_{x_2})^2}$, where η_1 and η_2 are constants.

3.1. Curvilinear Coordinates

In order to compute the sharp-interface limit, it is convenient to employ a curvilinear coordinate system $\{u^1, u^2, u^3\}$ that is based on the assumed limiting shape of the solid/liquid interface defined by the level curve $\phi = 1/2$, henceforth denoted as S. At any instant of time, the solid/liquid interface for $\epsilon = 0$ is expressed parametrically as $\vec{X}(u^1, u^2)$, where u^1 and u^2 provide a local coordinate description of the surface, as discussed in more detail in Appendix A. The transformation from the curvilinear coordinates to physical space is given by

$$\vec{x}(u^1, u^2, u^3) = \vec{X}(u^1, u^2) + u^3 \vec{n}(u^1, u^2), \tag{37}$$

where $\vec{n}$ is the normal to the interface at the point $\vec{X}(u^1, u^2)$. The interface therefore corresponds to the surface $u^3 = 0$. The transformation generates local contravariant basis vectors $\vec{e}_j = \partial \vec{x} / \partial u^j$ and an associated metric $g_{jk} = \vec{e}_j \cdot \vec{e}_k$. The partial derivatives of the transformation are denoted by $a^j_{\;k} = \partial x^j / \partial u^k$ and $b^k_{\;j} = \partial u^k / \partial x^j$; both are expressed as functions of the variables (u^1, u^2, u^3).

In the curvilinear coordinates the phase field is written as $\tilde{\phi}(u^1, u^2, u^3) = \phi(x^1, x^2, x^3)$. To simplify the notation, we denote the respective gradients by

$$p_j = \frac{\partial \phi}{\partial x^j}, \qquad \tilde{p}_k = \frac{\partial \tilde{\phi}}{\partial u^k}, \tag{38}$$

which transform as covariant vector components according to the law

$$p_j = b^k_{\;j} \tilde{p}_k. \tag{39}$$

In the curvilinear coordinates the transformed surface energy $\tilde{\gamma}$ is then obtained by inserting the expressions (39) into the function $\gamma(p_1, p_2, p_3)$; since $\tilde{\gamma}$ then has dependence not only on $\tilde{p}_k$ but also on u^k through the elements of the transformation matrix $b^k_{\;j}(u^1, u^2, u^3)$, the transformed surface energy is written in the form

$$\tilde{\gamma}(\tilde{p}_1, \tilde{p}_2, \tilde{p}_3, u^1, u^2, u^3) = \gamma(p_1, p_2, p_3). \tag{40}$$

Because the p_j variables depend linearly on $\tilde{p}_k$, $\tilde{\gamma}$ is seen to be a first-order homogeneous function of the variables $\tilde{p}_k$.

The transformed free-energy functional takes the form

$$\mathcal{F} = \int_V \left\{ 36\epsilon \tilde{\gamma}^2 + \frac{1}{4\epsilon} G(\tilde{\phi}) - P(\tilde{\phi}) u \right\} \sqrt{g} \, du^1 \, du^2 \, du^3, \tag{41}$$

where g denotes the determinant of the metric tensor and $\sqrt{g} \, du^1 \, du^2 \, du^3$ is the transformed volume element. The variation of $\mathcal{F}$ is given by

$$\frac{\delta \mathcal{F}}{\delta \tilde{\phi}} = -\frac{72\epsilon}{\sqrt{g}} \frac{\partial}{\partial u^k} \left(\sqrt{g} \, \tilde{\gamma} \frac{\partial \tilde{\gamma}}{\partial \tilde{p}_k} \right) + \frac{1}{4\epsilon} G'(\tilde{\phi}) - P'(\tilde{\phi}) u. \tag{42}$$

We set

$$\tilde{\xi}^k = \frac{\partial \tilde{\gamma}}{\partial \tilde{p}_k}; \tag{43}$$

each $\tilde{\xi}^k$ is a homogeneous function of the $\tilde{p}_k$ variables of degree zero. From the definition (40) it is seen that the variables $\tilde{\xi}^k$ form the contravariant components of the transformed ξ-vector; i.e., they satisfy the relation

$$\xi^j = a^j_{\;k} \tilde{\xi}^k. \tag{44}$$

The expression

$$\frac{1}{\sqrt{g}}\frac{\partial}{\partial u^k}\left(\sqrt{g}\,\tilde{\gamma}\tilde{\xi}^k\right) \tag{45}$$

is the divergence in curvilinear coordinates (see Appendix A) of the product of $\tilde{\gamma}$ and the ξ-vector.

4. The Limit $\epsilon \to 0$.

In the limit $\epsilon \to 0$, we expect the formation of a thin interfacial layer about the surface $\phi(x,y,z) = 1/2$ in which ϕ varies rapidly between zero and unity. We assume that the surface $\phi(x,y,z) = 1/2$ moves with normal velocity v_n into the liquid phase, given by $\phi = 1$.

In this anisotropic formulation of the phase-field equation, the main technical difficulty in conducting an asymptotic analysis lies in dealing with the term $\nabla \cdot (\gamma \vec{\xi})$ in the interfacial layer. We now examine its expansion in the interfacial layer.

4.1. Expansion of $\nabla \cdot (\gamma \vec{\xi})$

In the limit $\epsilon \to 0$ we anticipate the formation of an interfacial layer of thickness $\mathcal{O}(\epsilon)$. We therefore introduce the rescaled coordinate ρ, defined by $u^3 = \epsilon\rho$ and represent the phase field in this region as

$$\tilde{\phi} = \tilde{\phi}^{(0)}(u^1, u^2, \rho) + \epsilon\tilde{\phi}^{(1)}(u^1, u^2, \rho) + \mathcal{O}(\epsilon^2). \tag{46}$$

The inner expansion of the gradient of $\tilde{\phi}$ is then found to be

$$\nabla\phi = \frac{1}{\epsilon}\tilde{\phi}^{(0)}_{\rho}\vec{n} + \mathcal{O}(1). \tag{47}$$

We rewrite the divergence as the sum of three terms,

$$\frac{1}{\sqrt{g}}\sum_{k=1}^{3}\frac{\partial}{\partial u^k}\left(\sqrt{g}\,\tilde{\gamma}\tilde{\xi}^k\right) = \frac{1}{\sqrt{g}}\sum_{k=1}^{2}\frac{\partial}{\partial u^k}\left(\sqrt{g}\,\tilde{\gamma}\tilde{\xi}^k\right) + \frac{\partial(\tilde{\gamma}\tilde{\xi}^3)}{\partial u^3} + \frac{\tilde{\gamma}\tilde{\xi}^3}{\sqrt{g}}\frac{\partial\sqrt{g}}{\partial u^3}. \tag{48}$$

The inner expansion for this expression can be obtained using the intermediate results

$$\tilde{\gamma} = \frac{1}{\epsilon}\gamma(\vec{n})\tilde{\phi}^{(0)}_{\rho} + \gamma(\vec{n})\tilde{\phi}^{(1)}_{\rho} + \vec{\xi}(\vec{n})\cdot\nabla_S\tilde{\phi}^{(0)} + O(\epsilon), \tag{49}$$

$$\tilde{\xi}^3 = \gamma(\vec{n}) + O(\epsilon^2), \tag{50}$$

$$\frac{1}{\sqrt{g}}\frac{\partial\sqrt{g}}{\partial u^3} = \mathcal{K} + O(\epsilon) \tag{51}$$

that are derived in Appendix B; here $\gamma(\vec{n})$ and $\vec{\xi}(\vec{n})$ correspond to the surface energy and ξ-vector evaluated at the normal to the leading-order interface position, and are independent of ρ. The surface divergence operator also corresponds to the interface $\rho = 0$. We then have that

$$\epsilon \frac{\partial(\tilde{\gamma}\tilde{\xi}^3)}{\partial u^3} = \frac{1}{\epsilon}[\gamma(\vec{n})]^2 \tilde{\phi}_{\rho\rho}^{(0)} + [\gamma(\vec{n})]^2 \tilde{\phi}_{\rho\rho}^{(1)} + \gamma(\vec{n})\vec{\xi}(\vec{n}) \cdot \nabla_S \tilde{\phi}_{\rho}^{(0)} + O(\epsilon), \tag{52}$$

and

$$\frac{\epsilon}{\sqrt{g}} \sum_{k=1}^{2} \frac{\partial}{\partial u^k} \left(\sqrt{g}\,\tilde{\gamma}\tilde{\xi}^k \right) + \epsilon \frac{\tilde{\gamma}\tilde{\xi}^3}{\sqrt{g}} \frac{\partial \sqrt{g}}{\partial u^3} = \nabla_S \cdot \left\{ \gamma(\vec{n})\vec{\xi}(\vec{n})\tilde{\phi}_{\rho}^{(0)} \right\} + O(\epsilon). \tag{53}$$

We now go on to develop the solution for ϕ at each order in the interfacial layer.

4.2. Leading Order

The leading order problem for $\phi^{(0)}$ is

$$72[\gamma(\vec{n})]^2 \frac{\partial^2 \phi^{(0)}}{\partial \rho^2} - \frac{1}{4}G'(\phi^{(0)}) = 0, \tag{54}$$

where $G'(\phi) = 4\phi(\phi - 1)(\phi - 1/2)$, with boundary conditions

$$\phi^{(0)} \to 1 \text{ as } \rho \to +\infty, \text{ and } \phi^{(0)} \to 0 \text{ as } \rho \to -\infty. \tag{55}$$

Hence $\phi^{(0)}$ is given by the planar interface solution discussed above and so

$$\phi^{(0)}(u^1, u^2, \rho) = \frac{1}{2}\left[\tanh\left(\frac{\rho}{24\gamma(\vec{n})} \right) + 1 \right]. \tag{56}$$

The leading-order dimensionless surface energy is $\gamma(\vec{n})$, and

$$\int_{-\infty}^{\infty} [\phi_{\rho}^{(0)}]^2 d\rho \equiv \mathcal{I} = \frac{1}{72\gamma(\vec{n})}, \tag{57}$$

from which it follows that

$$\nabla_S \mathcal{I} = -\frac{\mathcal{I}}{\gamma(\vec{n})}\nabla_S\gamma(\vec{n}); \tag{58}$$

we shall use this identity below, when invoking the solvability condition.

4.3. First Order

The first order problem is

$$72[\gamma(\vec{n})]^2 \frac{\partial^2 \phi^{(1)}}{\partial \rho^2} - \frac{1}{4}G''(\phi^{(0)})\phi^{(1)} =$$

$$- 72\frac{\gamma(\vec{n})}{\mu(\vec{n})}v_n\phi_{\rho}^{(0)} - 72\,\gamma(\vec{n})\vec{\xi}(\vec{n}) \cdot \nabla_S\tilde{\phi}_{\rho}^{(0)} - 72\,\nabla_S \cdot \left\{ \gamma(\vec{n})\vec{\xi}(\vec{n})\tilde{\phi}_{\rho}^{(0)} \right\} - P'(\phi^{(0)})u, \tag{59}$$

where we have employed the homogeneity of γ and Eq. (47). Here $-v_n\phi_\rho^{(0)}$ is the leading order contribution obtained by transforming the time derivative $\epsilon\phi_t$ to the curvilinear coordinate system. The homogeneous adjoint solution to the linearised operator on the left-hand side is $\phi_\rho^{(0)}$. The solvability condition for this equation gives

$$u = -72\,\gamma(\vec{n})\vec{\xi}(\vec{n}) \cdot \int_{-\infty}^{\infty} \phi_\rho^{(0)} \nabla_S \tilde{\phi}_\rho^{(0)}\, d\rho - 72 \int_{-\infty}^{\infty} \phi_\rho^{(0)} \nabla_S \cdot \left\{ \gamma(\vec{n})\vec{\xi}(\vec{n})\tilde{\phi}_\rho^{(0)} \right\}\, d\rho - \frac{v_n}{\mu(\vec{n})}. \tag{60}$$

We have

$$72\,\gamma(\vec{n})\vec{\xi}(\vec{n}) \cdot \int_{-\infty}^{\infty} \phi_\rho^{(0)} \nabla_S \tilde{\phi}_\rho^{(0)}\, d\rho = 36\,\gamma(\vec{n})\vec{\xi}(\vec{n}) \cdot \nabla_S \int_{-\infty}^{\infty} [\phi_\rho^{(0)}]^2\, d\rho = \frac{-\vec{\xi}(\vec{n}) \cdot \nabla_S \gamma(\vec{n})}{2\gamma(\vec{n})}, \tag{61}$$

where we have employed the identity (58) in the last step. In a similar fashion we also find that

$$72 \int_{-\infty}^{\infty} \phi_\rho^{(0)} \nabla_S \cdot \left\{ \gamma(\vec{n})\vec{\xi}(\vec{n})\tilde{\phi}_\rho^{(0)} \right\}\, d\rho = \nabla_S \cdot \vec{\xi}(\vec{n}) + \frac{\vec{\xi}(\vec{n}) \cdot \nabla_S \gamma(\vec{n})}{2\gamma(\vec{n})}, \tag{62}$$

and the solvability condition (60) therefore simplifies to give

$$u = -\nabla_S \cdot \vec{\xi}(\vec{n}) - v_n/\mu(\vec{n}). \tag{63}$$

This is our principal result. It is the so-called Gibbs-Thomson-Herring equation expressed in term of the Cahn-Hoffman ξ-vector. It relates the dimensionless interface temperature u to the surface energy and interface kinetics.

5. Discussion

The ξ-vector formulation originally developed by Hoffman and Cahn was used in the context of a sharp interface model where it is a vector field with a domain restricted to the surface of the interface. We have shown above that the same ξ-vector arises naturally in phase-field models that describe a diffuse interface. In this setting the ξ-vector is defined throughout the whole domain as the vector field $\vec{\xi}(\vec{\nu})$, i.e., the ξ-vector at a point in space is given by the Hoffman-Cahn ξ-vector evaluated at the local normal $\vec{\nu}$ to the level curve of the phase field.

As noted in section 2 in the context of a sharp interface description,

$$\gamma(\vec{p}) = \vec{p} \cdot \vec{\xi}(\vec{p}), \tag{64}$$

where the normal vector to the interface is given by $\vec{n} = \vec{p}/|\vec{p}|$. This result also holds in the phase-field context in which $\vec{p}$ various throughout the domain, and $\vec{\nu} = \vec{p}/|\vec{p}|$ is the local normal to the phase-field

contours. Further, we note that along a curve $u^j = u^j(\omega)$, we have that

$$\frac{d\gamma}{d\omega} = \frac{\partial \tilde{\gamma}}{\partial \tilde{p}_k} \frac{d\tilde{p}_k}{d\omega} = \vec{\xi} \cdot \frac{d\vec{p}}{d\omega} \tag{65}$$

where $d\vec{p}/d\omega$ is the covariant derivative of $\vec{p}$ along the curve. Differentiating the identity (64) along the curve and using Eq. (65) yields

$$\vec{p} \cdot \frac{d\vec{\xi}}{d\omega} = 0, \tag{66}$$

where $d\vec{\xi}/d\omega$ is the covariant derivative of $\vec{\xi}$ along the curve. Eq. (64) to Eq. (66) are the extension of the fundamental relations of the ξ-vector given by Eq. (14) to Eq. (16) appropriate to the phase-field interpretation of the ξ-vector.

Finally, we provide a brief heuristic discussion of the relation of the surface divergence of the ξ vector to the Herring formula using the notation developed here. To do so, we consider a non-umbilic elliptic point [18] of the surface where both principal curvatures are positive. The coordinates are taken to lie along the lines of principal curvature, forming an orthogonal grid near the point. For these coordinates we then have $\vec{t}_1 \cdot \vec{t}_2 = 0$, and the derivatives of the normal vector are given by the Rodrigues formula [18]

$$\frac{\partial \vec{n}}{\partial u^1} = \mathcal{K}_1 \vec{t}_1, \qquad \frac{\partial \vec{n}}{\partial u^2} = \mathcal{K}_2 \vec{t}_2, \tag{67}$$

where $\mathcal{K}_1$ and $\mathcal{K}_2$ are the principal curvatures of the surface. This implies that in the surface the Christoffel symbols satisfy $\Gamma^3_{11} = -h_{11}\mathcal{K}_1$, $\Gamma^3_{22} = -h_{22}\mathcal{K}_2$, and $\Gamma^3_{12} = \Gamma^3_{21} = 0$ (see Eq. (92) in appendix A). We further assume that the surface metric tensor reduces to the unit matrix at this point, and that its first derivatives vanish there (corresponding to the surface coordinates satisfying a "local flatness" condition at this point, see [19]). Under these assumptions, the surface divergence of the ξ-vector at this point takes the form

$$\nabla s \cdot \vec{\xi} = \frac{\partial \tilde{\xi}^1}{\partial u^1} + \frac{\partial \tilde{\xi}^2}{\partial u^2} + (\mathcal{K}_1 + \mathcal{K}_2)\gamma. \tag{68}$$

For this point, it also follows from Eq. (102) in Appendix B that for $\vec{p} = \vec{n}$ and $u^3 = 0$ we have

$$\frac{\partial \tilde{\gamma}}{\partial u^1} = -\Gamma^3_{1m} \frac{\partial \tilde{\gamma}}{\partial \tilde{p}_m} = \mathcal{K}_1 \tilde{\xi}^1, \qquad \frac{\partial \tilde{\gamma}}{\partial u^2} = -\Gamma^3_{2m} \frac{\partial \tilde{\gamma}}{\partial \tilde{p}_m} = \mathcal{K}_2 \tilde{\xi}^2, \tag{69}$$

so that the surface divergence can be written in the form

$$\nabla s \cdot \vec{\xi} = \frac{\partial}{\partial u^1} \left\{ \frac{1}{\mathcal{K}_1} \frac{\partial \tilde{\gamma}}{\partial u^1} \right\} + \frac{\partial}{\partial u^2} \left\{ \frac{1}{\mathcal{K}_2} \frac{\partial \tilde{\gamma}}{\partial u^2} \right\} + \gamma(\mathcal{K}_1 + \mathcal{K}_2). \tag{70}$$

Defining new coordinates $\theta_1(u^1)$ and $\theta_2(u^2)$ by

$$\frac{d\theta_1}{du^1} = \mathcal{K}_1, \qquad \frac{d\theta_2}{du^2} = \mathcal{K}_2 \tag{71}$$

gives that

$$\nabla_S \cdot \vec{\xi} = \mathcal{K}_1 \left(\gamma(\vec{n}) + \frac{\partial^2 \gamma(\vec{n})}{\partial \theta_1^2} \right) + \mathcal{K}_2 \left(\gamma(\vec{n}) + \frac{\partial^2 \gamma(\vec{n})}{\partial \theta_2^2} \right). \tag{72}$$

This expression inserted into Eq. (63) gives the extension of the formula due to Herring [11] for the temperature of a moving curved interface.

6. Conclusions

The gradient energy term in an anisotropic phase-field model of the general type discussed by Kobayashi [4] can be formulated in terms of the surface energy $\gamma(\vec{n})$. The variation of the resulting free energy functional is easily computed if the argument of the surface energy has been extended to vectors of arbitrary magnitude as a homogeneous function of first degree [9, 10]. The resulting variational equation for the phase field contains the ξ-vector of Hoffman and Cahn [7, 8]. A formal asymptotic analysis of the sharp interface limit [5, 17] recovers the Gibbs-Thomson-Herring equation [11], in this case expressed in terms of the surface divergence of the ξ-vector.

We have assumed that the surface tension anisotropy is mild enough that missing orientations do not occur in the Gibbs-Wulff construction. The recognition that the phase-field equations can be formulated in terms of the ξ-vector provides a natural setting in which to investigate the way in which a phase-field model can describe the situation in which missing orientations and facets would be present in a sharp-interface model as well for the development of weak solutions and associated numerical methods. These are lines of research currently in hand.

7. Acknowledgments

A. Differential Geometry Results

Here we summarise some results from the differential geometry of surfaces; for more details, see, e.g., [20, 21].

A.1. The Surface Divergence

We consider a surface expressed parametrically in the form

$$\vec{x} = \vec{X}(u^1, u^2). \tag{73}$$

where u^1 and u^2 are general curvilinear coordinates for the surface. Contravariant basis vectors $\vec{t}_1$ and $\vec{t}_2$ for the tangent plane to the surface at any point are given by the partial derivatives

$$\vec{t}_1(u^1, u^2) = \frac{\partial \vec{X}}{\partial u^1}, \qquad \vec{t}_2(u^1, u^2) = \frac{\partial \vec{X}}{\partial u^2}. \tag{74}$$

The element of arclength ds along the surface is defined by

$$ds^2 = h_{11}du^1\,du^1 + 2h_{12}du^1\,du^2 + h_{22}du^2\,du^2, \tag{75}$$

where

$$h_{11} = \vec{t}_1 \cdot \vec{t}_1, \qquad h_{12} = h_{21} = \vec{t}_1 \cdot \vec{t}_2, \qquad h_{22} = \vec{t}_2 \cdot \vec{t}_2 \tag{76}$$

form the covariant components of the surface metric tensor whose determinant is $h = h_{11}h_{22} - (h_{12})^2 = |\vec{t}_1 \times \vec{t}_2|^2$. The normal vector to the surface can be written in the form

$$\vec{n}(u^1, u^2) = \frac{1}{\sqrt{h}}\vec{t}_1 \times \vec{t}_2. \tag{77}$$

The covariant basis vectors form a reciprocal basis set and are given by

$$\vec{t}^{\,1} = \frac{-1}{\sqrt{h}}\vec{n} \times \mathrm{t}_2 = \frac{1}{h}\left(h_{22}\vec{t}_1 - h_{12}\vec{t}_2\right), \quad \vec{t}^{\,2} = \frac{1}{\sqrt{h}}\vec{n} \times \mathrm{t}_1 = \frac{1}{h}\left(-h_{12}\vec{t}_1 + h_{11}\vec{t}_2\right). \tag{78}$$

The operator ∇_S can then be formally defined by

$$\nabla_S = \vec{t}^{\,1}\frac{\partial}{\partial u^1} + \vec{t}^{\,2}\frac{\partial}{\partial u^2}, \tag{79}$$

so a scalar function $f(u^1, u^2)$ defined on the surface has a surface gradient given by

$$\nabla_S f = \vec{t}^{\,1}\frac{\partial f}{\partial u^1} + \vec{t}^{\,2}\frac{\partial f}{\partial u^2}, \tag{80}$$

which is seen to be a covariant representation of the vector $\nabla_S f$. The surface divergence of the position vector $\vec{X}(u^1, u^2)$ is seen to be

$$\nabla_S \cdot \vec{X} = \vec{t}^{\,1} \cdot \frac{\partial \vec{X}}{\partial u^1} + \vec{t}^{\,2} \cdot \frac{\partial \vec{X}}{\partial u^2} = \vec{t}^{\,1} \cdot \vec{t}_1 + \vec{t}^{\,2} \cdot \vec{t}_2 = 2. \tag{81}$$

More generally, it can be shown [20, 21] that the surface divergence of a vector $\vec{A}(u^1, u^2)$ written in contravariant form

$$\vec{A}(u^1, u^2) = A^1(u^1, u^2)\vec{t}_1 + A^2(u^1, u^2)\vec{t}_2 + A^3(u^1, u^2)\vec{n}, \tag{82}$$

can be expressed as

$$\nabla_S \cdot \vec{A} = \frac{1}{\sqrt{h}} \left\{ \frac{\partial(\sqrt{h} A^1)}{\partial u^1} + \frac{\partial(\sqrt{h} A^2)}{\partial u^2} \right\} + A^3 \mathcal{K}, \tag{83}$$

where $\mathcal{K}$ is the mean curvature of the interface. In particular, taking $\vec{A} = \vec{n}(u^1, u^2)$, this expression shows that $\mathcal{K}$ is given by the surface divergence of the normal vector.

A.2. Surface-Fitted Coordinates

We next extend the coordinate system given above to provide coordinates in a neighbourhood of the surface. To do this, we introduce a third coordinate in the direction of the normal vector, and express a general position vector $\vec{x}$ as

$$\vec{x}(u^1, u^2, u^3) = \vec{X}(u^1, u^2) + u^3 \vec{n}(u^1, u^2), \tag{84}$$

This generates the contravariant basis vectors (see, e.g., [21]) given by

$$\vec{e}_1(u^1, u^2, u^3) = \frac{\partial \vec{x}}{\partial u^1} = \frac{\partial \vec{X}}{\partial u^1} + u^3 \frac{\partial \vec{n}}{\partial u^1} = \vec{t}_1(u^1, u^2) + u^3 \frac{\partial \vec{n}}{\partial u^1}, \tag{85}$$

$$\vec{e}_2(u^1, u^2, u^3) = \frac{\partial \vec{x}}{\partial u^2} = \frac{\partial \vec{X}}{\partial u^2} + u^3 \frac{\partial \vec{n}}{\partial u^2} = \vec{t}_2(u^1, u^2) + u^3 \frac{\partial \vec{n}}{\partial u^2},$$

$$\vec{e}_3(u^1, u^2) = \frac{\partial \vec{x}}{\partial u^3} = \vec{n}(u^1, u^2). \tag{86}$$

The j-th element of the vector $\vec{e}_k$ is denoted by $a^j_{\;k}(u^1, u^2, u^3)$, where $a^j_{\;k} = \partial x^j / \partial u^k$. The covariant components of the associated metric tensor are given by

$$g_{jk} = \vec{e}_j \cdot \vec{e}_k, \tag{87}$$

and we note that for this particular coordinate system that $\vec{e}_1 \cdot \vec{e}_3 = \vec{e}_2 \cdot \vec{e}_3 = 0$ and $\vec{e}_3 \cdot \vec{e}_3 = 1$.

The differential operator ∇ can be written in the form

$$\nabla = \vec{e}^{\,k} \frac{\partial}{\partial u^k}, \tag{88}$$

where here $\{\vec{e}^{\,k}\}$ are the covariant basis vectors related to the covariant basis vectors by

$$\mathbf{e}^1 = \frac{\mathbf{e}_2 \times \mathbf{e}_3}{(\mathbf{e}_1 \cdot \mathbf{e}_2 \times \mathbf{e}_3)}, \qquad \mathbf{e}^2 = \frac{\mathbf{e}_1 \times \mathbf{e}_3}{(\mathbf{e}_2 \cdot \mathbf{e}_1 \times \mathbf{e}_3)}, \qquad \mathbf{e}^3 = \frac{\mathbf{e}_1 \times \mathbf{e}_2}{(\mathbf{e}_3 \cdot \mathbf{e}_1 \times \mathbf{e}_2)}. \qquad (89)$$

We denote the determinant of the metric tensor by g, which also satisfies $(\mathbf{e}_1 \cdot \mathbf{e}_2 \times \mathbf{e}_3) = \sqrt{g}$. For the coordinate system considered here, we have $\mathbf{e}^3 = \mathbf{e}_3 = \vec{n}(u^1, u^2)$. The gradient of a scalar function $\tilde{\phi}(u^1, u^2, u^3) = \phi(x^1, x^2, x^3)$ then has the form

$$\nabla \phi = \vec{e}^{\,k} \frac{\partial \tilde{\phi}}{\partial u^k} \qquad (90)$$

In applying ∇ to a vector field, one must differentiate the basis vectors as well as the coefficients. The covariant derivatives of the covariant basis vectors satisfy

$$\frac{\partial \vec{e}^{\,j}}{\partial u^k} + \Gamma^j{}_{mk} \vec{e}^{\,m} = 0, \qquad (91)$$

where $\Gamma^j{}_{mk}$ are Christoffel symbols defined by

$$\Gamma^j{}_{mk} = -\vec{e}_m \cdot \frac{\partial \vec{e}^{\,j}}{\partial u^k} = -a^r{}_m \frac{\partial b^j{}_r}{\partial u^k}. \qquad (92)$$

For the coordinate system considered here, we have

$$\Gamma^3{}_{3k} = -\vec{n} \cdot \frac{\partial \vec{n}}{\partial u^k} = 0. \qquad (93)$$

For a vector field $\vec{A}$ expressed in contravariant form,

$$\vec{A}(u^1, u^2, u^3) = A^j(u^1, u^2, u^3)\vec{e}_j, \qquad (94)$$

it can be shown [21] that its divergence is

$$\nabla \cdot \vec{A} = \frac{1}{\sqrt{g}} \frac{\partial(\sqrt{g} A^j)}{\partial u^j}. \qquad (95)$$

Note that for $u^3 = 0$ we have $\vec{e}_1 = \vec{t}_1$, $\vec{e}_2 = \vec{t}_2$, and $g = h$.

Comparing the expression (95) with the result of applying (88) to the vector $\vec{A} = \vec{n}(u^1, u^2)$, for which $A^1 = A^2 = 0$ and $A^3 = 1$, gives

$$\frac{1}{\sqrt{g}} \frac{\partial \sqrt{g}}{\partial u^3}\bigg|_{u^3=0} = \left(\vec{e}^{\,1} \cdot \frac{\partial \vec{n}}{\partial u^1} + \vec{e}^{\,2} \cdot \frac{\partial \vec{n}}{\partial u^2} \right)\bigg|_{u^3=0} = \vec{t}^{\,1} \cdot \frac{\partial \vec{n}}{\partial u^1} + \vec{t}^{\,2} \cdot \frac{\partial \vec{n}}{\partial u^2} = \nabla_S \cdot \vec{n} = \mathcal{K}, \qquad (96)$$

where $\mathcal{K}$ is the mean curvature of the surface $u^3 = 0$ as discussed above. We therefore have that

$$\nabla \cdot \vec{A}\bigg|_{u^3=0} = \frac{1}{\sqrt{h}} \sum_{j=1}^{2} \frac{\partial[\sqrt{h} A^j(u^1, u^2, 0)]}{\partial u^j} + A^3(u^1, u^2, 0)\mathcal{K} + \frac{\partial A^3}{\partial u^3}\bigg|_{u^3=0}$$

$$= \nabla_S \cdot \vec{A}(u^1, u^2, 0) + \frac{\partial A^3}{\partial u^3}\bigg|_{u^3=0}. \qquad (97)$$

B. Some Asymptotic Results

In this appendix we give derive asymptotic representations of γ and $\vec{\xi}$ in the interfacial layer.

The inner expansion of $\tilde{\gamma} = \tilde{\gamma}(\tilde{p}_1, \tilde{p}_2, \tilde{p}_3, u^1, u^2, u^3)$ is obtained by writing

$$\tilde{\gamma} = \tilde{\gamma}\left(\frac{\partial\tilde{\phi}}{\partial u^1}, \frac{\partial\tilde{\phi}}{\partial u^2}, \frac{1}{\epsilon}\frac{\partial\tilde{\phi}}{\partial\rho}, u^1, u^2, \epsilon\rho\right) = \frac{1}{\epsilon}\tilde{\gamma}\left(\epsilon\frac{\partial\tilde{\phi}}{\partial u^1}, \epsilon\frac{\partial\tilde{\phi}}{\partial u^2}, \frac{\partial\tilde{\phi}}{\partial\rho}, u^1, u^2, \epsilon\rho\right), \tag{98}$$

where we have used the fact that $\tilde{\gamma}$ is first-degree homogeneous in the partial derivatives of $\tilde{\phi}$. Inserting the expansion $\tilde{\phi} = \tilde{\phi}^{(0)} + \epsilon\tilde{\phi}^{(1)} + O(\epsilon^2)$ gives

$$\tilde{\gamma} = \frac{1}{\epsilon}\left\{\tilde{\gamma}\left(0, 0, \tilde{\phi}_\rho^{(0)}, u^1, u^2, 0\right) + \epsilon\left[\tilde{\phi}_{u^1}^{(0)}\tilde{\gamma}_{\tilde{p}_1} + \tilde{\phi}_{u^2}^{(0)}\tilde{\gamma}_{\tilde{p}_2} + \tilde{\phi}_\rho^{(1)}\tilde{\gamma}_{\tilde{p}_3} + \rho\tilde{\gamma}_{u^3}\right] + O(\epsilon^2)\right\}, \tag{99}$$

where the partial derivatives of $\tilde{\gamma}$ are all evaluated with the argument list $(0, 0, \tilde{\phi}_\rho^{(0)}, u^1, u^2, 0)$. From homogeneity we have

$$\tilde{\gamma}\left(0, 0, \tilde{\phi}_\rho^{(0)}, u^1, u^2, 0\right) = \tilde{\phi}_\rho^{(0)}\tilde{\gamma}\left(0, 0, 1, u^1, u^2, 0\right) \equiv \tilde{\phi}_\rho^{(0)}\gamma(\vec{n}), \tag{100}$$

where the latter equality follows from the observation that $\tilde{p}_1 = \tilde{p}_2 = 0$ and $\tilde{p}_3 = 1$ are the components of the normal vector $\vec{n}(u^1, u^2)$. It also follows that

$$\tilde{\gamma}_{P_3}\left(0, 0, \tilde{\phi}_\rho^{(0)}, u^1, u^2, 0\right) = \gamma(\vec{n}). \tag{101}$$

A calculation shows that

$$\frac{\partial\tilde{\gamma}}{\partial u^r}(\tilde{p}_1, \tilde{p}_2, \tilde{p}_3, u^1, u^2, u^3) = \frac{\partial\gamma}{\partial p_j}\frac{\partial b^k_{\,j}}{\partial u^r}\tilde{p}_k$$

$$= a^j_{\,m}\tilde{\xi}^m\frac{\partial b^k_{\,j}}{\partial u^r}\tilde{p}_k = -\Gamma^k_{\,mr}\tilde{\xi}^m\,\tilde{p}_k. \tag{102}$$

Therefore

$$\frac{\partial\tilde{\gamma}}{\partial u^3}(0, 0, \tilde{p}_3, u^1, u^2, 0) = -\Gamma^3_{\,m3}\tilde{\xi}^m\,\tilde{p}_3 = 0, \tag{103}$$

since, as noted in Appendix A, $\Gamma^3_{\,m3} = 0$ in this coordinate system. The remaining term can be written in the form

$$\tilde{\phi}_{u^1}^{(0)}\tilde{\gamma}_{\tilde{p}_1}(0, 0, \tilde{\phi}_\rho^{(0)}, u^1, u^2, 0) + \tilde{\phi}_{u^2}^{(0)}\tilde{\gamma}_{\tilde{p}_2}(0, 0, \tilde{\phi}_\rho^{(0)}, u^1, u^2, 0) = \vec{\xi}^{(0)} \cdot \nabla_S\tilde{\phi}^{(0)}, \tag{104}$$

where the leading-order components $\tilde{\xi}_j^{(0)}$ of the ξ-vector for $j = 1$ and $j = 2$ are

$$\tilde{\xi}_j^{(0)} = \tilde{\gamma}_{\tilde{p}_j}(0, 0, 1, u^1, u^2, 0); \tag{105}$$

here we have used the homogeneity of $\tilde{\gamma}_{\tilde{p}_j}$. Together with (101), this shows that $\tilde{\xi}_j^{(0)}$ are the curvilinear components of the vector $\vec{\xi}(\vec{n})$, so that to leading order the ξ-vector depends only on u^1 and u^2.

The expansion of $\tilde{\gamma}$ can therefore be written in the form

$$\tilde{\gamma} = \frac{1}{\epsilon}\gamma(\vec{n})\tilde{\phi}_\rho^{(0)} + \left[\vec{\xi}(\vec{n}) \cdot \nabla_S\tilde{\phi}^{(0)} + \gamma(\vec{n})\tilde{\phi}_\rho^{(1)}\right] + O(\epsilon). \tag{106}$$

The inner expansion of $\tilde{\xi}^3$ is required through first order, and is obtained by writing

$$\tilde{\xi}^3 = \frac{\partial\tilde{\gamma}}{\partial\tilde{p}_3}\left(\epsilon\tilde{\phi}_{u^1}, \epsilon\tilde{\phi}_{u^2}, \tilde{\phi}_\rho, u^1, u^2, \epsilon\rho\right). \tag{107}$$

Expanding in ϵ gives

$$\tilde{\xi}^3 = \tilde{\gamma}_{p_3}\left(0, 0, \tilde{\phi}_\rho^{(0)}, u^1, u^2, 0\right) + \epsilon\left\{\tilde{\phi}_{u^1}^{(0)}\tilde{\gamma}_{\tilde{p}_1\tilde{p}_3} + \tilde{\phi}_{u^2}^{(0)}\tilde{\gamma}_{\tilde{p}_2\tilde{p}_3} + \tilde{\phi}_\rho^{(1)}\tilde{\gamma}_{\tilde{p}_3\tilde{p}_3} + \rho\tilde{\gamma}_{u^3\tilde{p}_3}\right\} + O(\epsilon^2), \tag{108}$$

where the second derivatives of $\tilde{\gamma}$ are all evaluated with the argument list $(0, 0, \tilde{\phi}_\rho^{(0)}, u^1, u^2, 0)$. As shown above, the first term is $\gamma(\vec{n})$. Differentiating the identity

$$\tilde{\gamma}_{p_j}\left(0, 0, \lambda\tilde{p}_3, u^1, u^2, 0\right) = \tilde{\gamma}_{p_j}\left(0, 0, \tilde{p}_3, u^1, u^2, 0\right) \tag{109}$$

with respect to λ shows that $\tilde{\gamma}_{\tilde{p}_j\tilde{p}_3}(0, 0, \tilde{p}_3, u^1, u^2, 0) = 0$. Finally, since $\tilde{\gamma}_{u^3}(0, 0, \tilde{p}_3, u^1, u^2, 0) = 0$ as shown above, we also have that $\tilde{\gamma}_{u^3\tilde{p}_3}$ vanishes as well. Therefore there is no first-order correction for $\tilde{\xi}^3$ and we have

$$\tilde{\xi}^3 = \gamma(\vec{n}) + O(\epsilon^2). \tag{110}$$

We also note that Eq. (96) implies the inner expansion

$$\frac{1}{\sqrt{g}}\frac{\partial\sqrt{g}}{\partial u^3}\bigg|_{u^3=\epsilon\rho} = \mathcal{K} + O(\epsilon). \tag{111}$$

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